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CERTIFICATE

This certificate is issued in support of an application for Patent registration in a country outside New Zealand pursuant to the Patents Act 1953 and the Regulations thereunder.

I hereby certify that annexed is a true copy of the Provisional Specification as filed on 18 June 2003 with an application for Letters Patent number 526561 made by ANTHONY DAVID WOOLHOUSE.

I further certify that pursuant to a claim under Section 24(1) of the Patents Act 1953, a direction was given that the application proceed in the name of INDUSTRIAL RESEARCH LIMITED.

Dated 23 June 2004.

Neville Harris
Commissioner of Patents, Trade Marks and Designs

COMMISSIONER OF PATENTS, TRADEMARKS & DESIGNS
NEW ZEALAND

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PROVISIONAL SPECIFICATION

ZWITTERIONIC NON-LINEAR OPTOPHORES AND DEVICES INCORPORATING THESE

WE, ANTHONY DAVID WOOLHOUSE, a New Zealand citizen of 21 Harbour View Road, Northland, Wellington, New Zealand, and ANDREW JOHN KAY, a New Zealand citizen of 23 Moa Street, Alicetown, Lower Hutt, Wellington, New Zealand do hereby declare this invention to be described in the following statement:

TECHNICAL FIELD

The present invention relates to a new class of second order non-linear optophores (optical chromophores) and processes for making them. The invention also relates to polymers containing the optical chromophores and devices incorporating the same.

BACKGROUND OF THE INVENTION

In recent years there has been intense interest in molecules displaying large and efficient nonlinear optical responses (μ.ß) and in the electro-optic materials that permit the effective translation of these molecular properties into large, efficient and usable macroscopic responses. This interest is due to their potential application in emerging optoelectronic and photonic technologies.

Such materials contain molecules with highly polarisable electrons. The application of an electric field changes the electron polarisation, causing in an increase in the index of refraction. The resulting decrease in the velocity of light can be used to convert electric signals into optical signals.

In attempting to design all-plastic (i.e., all organic/polymeric) composite materials as active components of optoelectronic devices, a number of criteria need to be addressed. Ideally, the active molecules should display a large nonlinear optical response while still retaining synthetic expediency, transparency at communications wavelengths, and compatibility either when doped or functionalised within a polymer matrix. The composite materials must also exhibit thermal and photostability and maintain the noncentrosymmetry of the poled optophore array (i.e. temporal stability of the EO effect).

As these properties are interrelated, the structural features of a molecule that optimise one property may attenuate another. Accordingly, there continues to be a need for suitable optophores with improved properties.

Generally, optophores comprise donor (D) and acceptor (A) nuclei flanking a large, conjugated p-manifold which may contain auxilliary substituents to minimise potentially

deleterious aggregation effects that occur when the compounds are constrained within a matrix.

Conventional optophores are based upon 'left-hand-side' (LHS) systems (Marder-Perry plot) in which the ground-state electron distributions are dominated by only modest levels of charge separation or 'bond length alternation'. Such compounds are known to demonstrate positive solvatochromic behaviour ($\mu.\beta_o$) primarily as a result of the hyperpolarisabilty term ß.

For example, US 6,067,186 describes compounds characterised as having tetherable N,N-dialkyanilino or N,N-dialkylaminothiopheno donor functionalities linked via a p-electron interconnect to heterocyclic systems that act as electron acceptors. Large pendant substituents may be placed on either or both the interconnect or the electron acceptor heterocycle.

In contrast, optophores whose ground states are predominated by 'zwitterionic' electron distributions ('right-hand-side' (RHS) optophores,) are expected to possess large ground-state dipole moments. This is considered to prevent efficient maximisation of macroscopic 'material' optical non-linearity as a result of unfavourable optophore dipole-dipole interactions during poling. As a result, those skilled in the art expect 'right-hand-side' optophores to be less useful in optoelectronic applications.

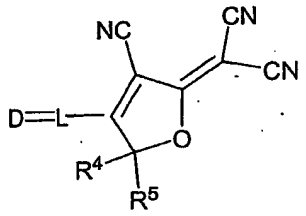
Surprisingly, it has been discovered that the zwitterionic non-linear optophores of the present invention achieve large molecular figures of merit ($\mu.\beta$) and are suitable for construction into polymer compositions which have application in optoelectronic and photonic technologies.

Accordingly, it is an object of the present invention to provide optophores with improved physical properties which also display a large and efficient nonlinear optical response or at least to provide the public with a useful choice.

SUMMARY OF THE INVENTION

The present invention relates to a new class of zwitterionic non-linear optophores comprising a heteroaromatisable donor nucleus (D) connected to a cyanodicyanovinyldihydrofuran acceptor (A) via a substituted polyenic linker (L) and synthesis of same. The donor nuclei are selected from quinolinylidene (Q), pyridinylidene (PY) and benzothiazolidinylidene (BT) groups.

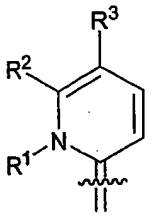
In one aspect the invention provides a compound of the general Formula I:



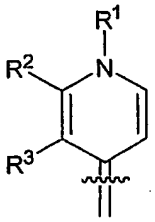
I

wherein:

D is selected from the group comprising

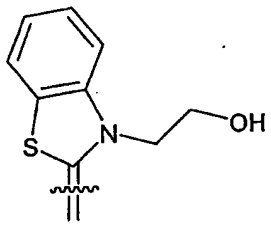


Q



PY

and



BT

wherein:

R^1 is alkyl or hydroxyalkyl;

R^2 and R^3 are H, or together form a 6-membered aromatic ring;

L is an optionally substituted conjugated polyenic chain of 3 to 7 carbon atoms; and

R^4 and R^5 are independently alkyl, hydroxyalkyl or p-C_6H_4-OAc.

Preferably, L is an optionally substituted conjugated polyenic chain of 3 to 5 carbon atoms.

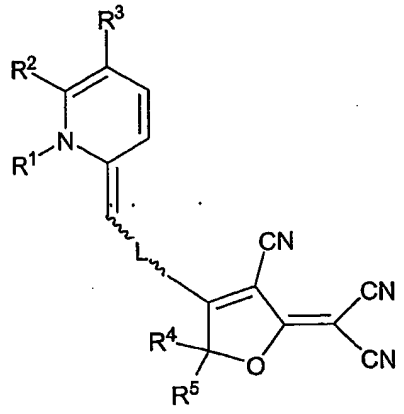
Optionally, substituents may be added to the chain so as to minimise optophore dipole-dipole interactions and/or to rigidify the linker. These substituents may form cyclic structures with the p-electron backbone of the linker group.

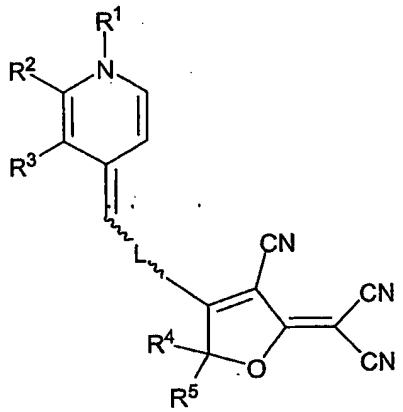
Preferably, R^1 is hydroxyalkyl;

Preferably, R^2 and R^3 together form a 6-membered aromatic ring;

Preferably, R^4 and R^5 are independently alkyl or hydroxyalkyl.

Particularly preferred are compounds of the Q and PY series:





wherein

R^1 is CH_3, CH_2CH_2OH, $CH_2CH(OH)CH_2OH$;

R^2 and R^3 are H, or together form a 6-membered aromatic ring;

One of R^4 or R^5 is hydroxyalkyl;

and L is an optionally substituted polyenic chain of 5 carbon atoms.

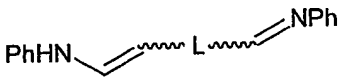
In particularly preferred compounds, R_1 is dihydroxyalkyl. The provision of two hydroxyl groups allows the optophores of the invention to be used in the synthesis of new polyurethane, polycarbonate and polyamic acid/polyimide polymers.

The hydroxyalkyl group at $R^4$and/or R^5 facilitates crosslinking of the polymers.

In another aspect the invention provides a method of preparing a compound of Formula I comprising:

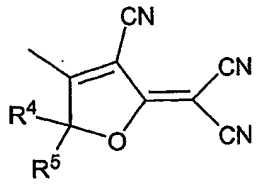
(a) reacting a compound of Formula II:

II

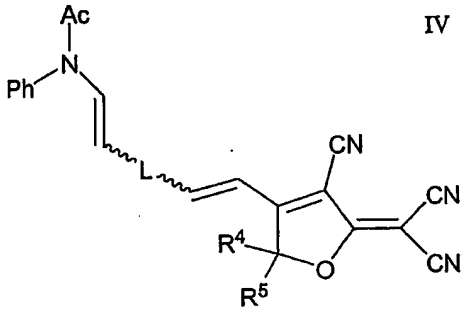


wherein L is defined as above, with a compound of Formula III:

III

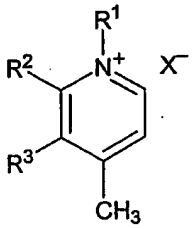


wherein R^4 and R^5 are as defined above, to form a compound of Formula IV:

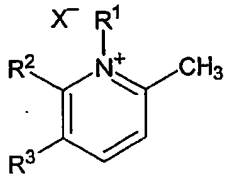


IV

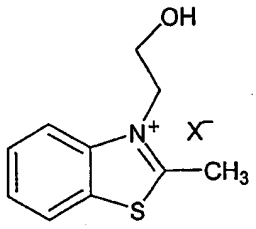
(b) reacting the compound of Formula IV from step (a) with an azinium or azolium donor derivative of Formula V, VI, or VII , where X is halogen, to form a compound of Formula I.



V



VI



VII

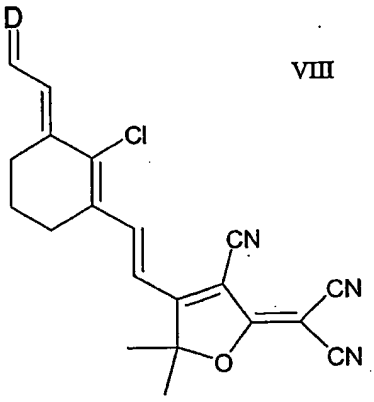
Each of the above mentioned steps is described in greater detail below.

Preferably, step (a) is performed in acetic anhydride, however other solvents may be used such as methanol.

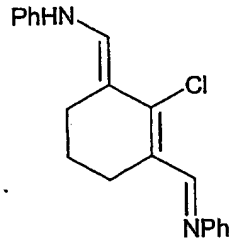
The (oligo)enamido dihydrofuran acceptor of Formula III is preferably reacted with an equimolar amount of a compound of Formula II. An equivalent of sodium acetate may also be added when a bisanil hydrochloride is used.

The donor derivatives IV, V and VI can be prepared using standard methods known in the art. Preferably, step (b) is performed by reacting stoichiometric quantities of each of the donor and acceptor components in refluxing acetic anhydride for 10 minutes. Preferably, the acetic anhydride contains an equivalent of triethylamine. Those skilled in the art will appreciate that other solvents and/or bases may be used in the method, and that the reaction time may differ depending on the nature of the reactants.

Substitution of the linker component can be achieved by modifying the bisanil component prior to reaction with the cyanodicyanovinyldihydrofuran acceptor of Formula III. For example, compounds wherein the linker comprises an alkylcycloalkenyl moiety (Formula VIII) can be accessed using the chlorocyclohexene dialdehyde bisanil of Formula IX,



VIII



IX

Using this methodology, optophores of Formula I incorporating a variety of different linker structures can be accessed by utilising the correct bisanil derivative.

Compounds displaying $\mu_{calc}\ \beta_{o(HRS)}$ values in excess of 15 000 x 10^{-48} esu are considered to possess exceptional optical nonlinearity. The optophores of the present invention give μ_{calc}

$\beta_{o(HRS)}$ values of up to 9384 x 10^{-48} esu, therefore show great potential for use in optoelectronic applications.

In a further aspect the invention provides a composite material comprising

(a) a compound of formula I; and

(b) a polymer material

The polymer material can be a homopolymer or a co-polymer.

More preferably, the polymer material comprises polyurethane, polycarbonate, polyamic acid/ polyimide.

In a yet further aspect the invention provides an optoelectronic device comprising the composite material of the invention.

The devices may include single elements or arrays of phase and amplitude optical modulators formed from the composite materials of the invention.

The functions of such devices include, but are not limited to: electrical to optical signal transduction; radio wave to millimeter wave electromagnetic radiation (signal) detection; radio wave to millimeter wave electromagnetic generation (broadcasting); optical and millimeter wave bean steering; and signal processing such as analog to digital conversion, ultrafast switching of signals at nodes of optical networks, and highly precise phase control of optical and millimeter wave signals.

The composite materials of the invention can be fabricated into a wide range of optoelectronic devices using standard protocols known in the art. Many articles and patents describe suitable techniques.

The invention also provides a method of data transmission comprising transmitting light through a composite material of the invention.

Those skilled in the art will appreciate that various adaptions and modifications of the preferred embodiments can be configured without departing from the scope and spirit of the invention. Therefore, it is to be understood that the invention may be practices other than as specifically described herein.

EXAMPLES

General Information

^{1}H- and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300MHZ spectrometer and proton multiplicities are defined by the usual notations. The assignments of resonances were made employing DEPT, COSY, HSQC and NOESY pulse sequences.

Uv-vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer and accurate mass measurements were made on a PE Biosystems Mariner mass spectrometer operating in the electrospray mode. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand and melting points are uncorrected.

The apparatus and experimental procedures for measuring hyper-Raleigh scattering (HRS) were exactly as described previously. β values were determined by using $ß_{800}$ for crystal violet chloride (338×10^{-30} esu in methanol) as an external reference. All measurements were performed in DMSO and optical local field correction factors were applied.

Uv-vis spectral characterisation

The electronic absorption spectra of the optophores from all PY, Q and BT series show intense charge-transfer absorption maxima in the 500 – 850 nm range and reveal the expected red shifts as the extent of conjugation is increased (Table 1). Significant windows of transparency exist in the 350-450 nm region of the spectrum. All compounds are negatively solvatochromic, a feature which qualitatively distinguishes these zwitterionic RHS systems from those 'belonging' to the LHS. The effect of benzannelation on $?_{max}$ of PY systems is quite pronounced, there being red shifts of up to 150 nm in going

from PY to Q, for example. The BT series shows not only the effects of benzannelation but also the effects of introducing a component of the p-interconnect which confers a degree of rigidity or configuration locking to the molecule. A compound containing the chlorocyclohexenylidene linkage is red-shifted by approximately 40 nm when compared to its iso-p-electronic series member containing a 7 carbon linker.

Table 2. Electronic absorption data for selected chromophores.

Compound	λ_{max} (DMF)	$\log_{10}\varepsilon$ (DMF)	λ_{max} (Methanol)	λ_{max} (Pyridine)	$\Delta\lambda_{max}$ (λ_{pyr}-λ_{MeOH})
4-pyr-form	570	4.86	564	600	36
4-pry-mal	600	4.78	592	670	78
4-pyr-glut	615	4.76	595	685	90
diOH-4-py-frm	572	4.79	570	598	28
diOH-4-py-mal	604	4.64	598	662	64
2-pyr-form	556	4.90	550	580	30
2-pyr-mal	588	4.81	582	662	80
2-pyr-glut	598	4.29	580	670	90
diOH-2-py-frm	556	4.72	552	578	26
diOH-2-py-mal	590	4.61	584	652	68
4-quin-form	660	5.00	654	682	28
4-quin-mal	735	4.88	724	782	58
4-quin-glut	735	4.70	705	860	155
4-quin-Cl-CH			710	865	115
2-quin-form	620	5.18	610	634	24
2-quin-mal	710	5.12	700	740	40
2-quin-glut	746	4.85	700	850	150
bt-form	605	5.18	598	614	16
bt-mal	705	5.21	698	718	20
bt-glut	810	4.91	805	830	25
bt-Cl-CH	854	4.91	840	865	25

Hyper Raleigh scattering studies

The first-order hyperpolarisabilities, ß, of a representative suite of these zwitterionic optophores have been measured using the HRS technique with a femtosecond-pulsed fundamental of 800 nm and SH at 400 nm, at which wavelength no two-photon-induced fluorescence was detected by temporal resolution of emitted light signals. The ß values are therefore true experimental values with no resonance enhancement. Furthermore, the resonance enhancement due to the fact that the CT band is in between the fundamental and the second harmonic indicates that the signs for the dynamic ß at the measurement wavelength and for the static $ß_o$ are opposite, this being based upon assumptions applied to the two-state model.

HRS derived ß and $ß_o$ values are presented in Table 2 together with calculated values of the ground-state dipole moment μ and $ß_o$ and the corresponding figures of merit (μ $ß_o$). In spite of the fact that 800 nm radiation triggered some (not unexpected) photodegradation of various of these optophores, the results clearly follow the expected trend which shows an increasing ß as a function of increasing conjugation length. Interestingly, the effects of benzannelation upon the PY systems; that is, in going from PY to Q, have a marked effect upon the size of $ß_o$. This is perhaps an indication of the increasing donor strength of Q systems over PY systems. To the extent that $ß_o$ values for the two BT compounds are reliable, then these data again suggest that the BT nucleus is midway in strength between the PY and Q donors, as some of our earlier findings had shown.

Inasmuch as comparisons of data acquired in different experimental regimes is meaningful, we note that the figures of merit (μ_{calc} $ß_{o(HRS)}$) we obtain for the longer PY and Q optophores (Table 2) are of the same order of magnitude as that reported for the optophores of US 6,067,186, members of which (LHS) class are characterised as having exceptional optical nonlinearities. The highest value of μ_{calc} $ß_{o(HRS)}$ reported for an optophore of US 6,067,186 is 8255×10^{-48} and those we obtain for the highest members of each of the PY and Q suites are 8900×10^{-48} and 9384×10^{-48} esu, respectively.

Table 2. Calculated and experimental values of β_o and μ, and the corresponding figures of merit.

Compound	μ^a (calc)	β_o^b (calc)	β_o^c (found)	$\mu_{(calc)}\beta_{o(calc)}$	$\mu_{(calc)}\beta_{o(found)}$
4-pyr-form	17.7	148	110	2620	1947
4-pry-mal	17.9	268	360	4749	6444
4-pyr-glut	17.8	343	500	6105	8900
2-pyr-form	15.6	125	-	1950	-
2-pyr-mal	15.9	240	-	3816	-
2-pyr-glut	15.9	319	-	5072	-
4-quin-form	15.5	153	440	2372	6820
4-quin-mal	12.7	229	560	2908	7112
4-pyr-glut	13.8	253	680	3491	9384
2-quin-form	14.7	142	-	2087	-
2-quin-mal	14.7	247	-	3631	-
2-quin-glut	14.6	309	-	4511	-
bt-form	10.4	100	240	1040	2496
bt-mal	12.9	173	260	2232	3354
bt-glut	12.8	213	-	2726	-

a MOPAC/AM1 using .....

b β is the dynamic first hyperpolarisability measured using the femtosecond-pulsed Ti-sapphire fundamental at 800 nm

c β_o is the static first hyperpolarisability estimated by using the two-state model

4-[-2-Anilinovinyl]-1-(2-hydroxyethyl)pyridinium iodide

A mixture of N-(2-hydroxyethyl)pyridinium iodide (24 g) and N,N'-diphenylformamidine (18 g) was stirred at 120 °C for 1 h. On cooling the mixture formed a dark tar. This was washed with 2 x 30 mL of ether and then allowed to stand, whereupon a brown-black solid formed. Recrystallisation from methanol afforded olive-green microcrystals (17.99 g; 54%), m.p. 192-193 °C. (Found: C; 48.94, H; 4.69 N; 7.94 $C_{15}H_{17}IN_2O$ requires C; 48.93, H; 4.65, N; 7.61 %). ^{1}H NMR (d_6-DMSO) d 10.30 (s, 1H), 8.50 (d, *J* 13.0 Hz, 1H), 8.33 (d, *J* 7.1 Hz, 2H), 7.77 (d, *J* 6.8 Hz, 2H), 7.33 (m, 4H), 7.03 (m, 1H), 5.89 (d, *J* 13.0 Hz, 1H), 5.13 (t, *J* 5.10 Hz, 1H), 4.30 (t, *J* 4.9 Hz, 2H), 3.78 (m, 2H). ^{13}C NMR (d_6-DMSO) 155.4

(C_Q), 142.9 (CH), 142.6 (CH), 140.9 (C_Q), 129.9 (CH), 123.0 (CH), 119.0 (CH), 116.2 (CH), 99.1 (CH), 60.7 (CH_2), 60.4 (CH_2). ?$_{max}$ (DMF) 428 $\log_{10}$e 4.82.

Synthesis of (N-acetyl-N-phenyl-*oligo*enamino)-2(5*H*)-furanylidene}propanedinitrile acceptors: General Condensation Procedure.

A mixture of the bisanil monohydrochloride (5.0 mmol), TCVDF(ref) (5.1 mmol) and anhydrous sodium acetate (5.1 mmol) in acetic anhydride was refluxed for 5 – 10 min before being allowed to cool and stand overnight. In the case of *N,N'*-diphenylformamidine free base, no sodium acetate was employed. Adducts were recovered by filtration as highly crystalline, coloured solids, and were washed with acetic anhydride (2x5 mL), followed by copious water and finally isopropanol. After drying in vacuum they were suitable for use without further purification.

{4-(2-Acetanilidoethenyl)-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile was purified by recrystallisation from acetone and isolated as yellow plates **(xx %)**, m.p. 274-278 °C (dec). (Found: C; 69.64, H; 4.57, N; 16.22. $C_{20}H_{16}N_4O_2$ requires C; 69.77, H; 4.65, N; 16.28 %); Found: MH^+ *m/z* 345.13460; $C_{20}H_{16}N_4O_2$ requires MH^+ *m/z* 345.13480; ? = 0.6 ppm). ^{1}H NMR (d_6-DMSO) d 8.72 (d, *J* 14.4 Hz, 1H), 7.63 (m, 3H), 7.47 (m, 2H), 5.10 (d, *J* 14.4 Hz, 1H), 2.05 (s, 3H), 1.66 (s, 6H). **^{13}C NMR (d_6-DMSO)** ?$_{max}$ (DMF) 430 $\log_{10}$e 4.74

{4-(4-Acetanilido-*trans*-1,3-butadienyl)-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}-propanedinitrile was purified by recrystallisation from acetone and isolated as brick-red crystalline solid **(xx %)**, m.p. 272-274 °C (dec). (Found: C; 71.22, H; 4.58, N; 15.01. $C_{22}H_{18}N_4O_2$ requires C; 71.35, H; 4.86, N; 15.14 %) Found: MH^+ *m/z* 371.15025; $C_{22}H_{18}N_4O_2$ requires MH^+ *m/z* 371.15141; ? = 3.1 ppm). ^{1}H NMR (d_6-DMSO) d 8.54 (d, *J* 13.3 Hz, 1H), 7.91 (dd, *J* 15.3, 11.2 Hz, 1H), 7.57 (m, 3H, aromatic), 7.40 (m, 2H, aromatic), 6.40 (d, *J* 15.4 Hz, 1H), 5.41 (dd, *J* 13.3, 11.2 Hz, 1H), 1.99 (s, 3H), 1.70 (s, 6H). ^{13}C NMR (d_6-DMSO) 177.5 (C_Q), 176.3 (C_Q), 169.7 (C_Q), 151.4 (CH), 145.3 (CH), 138.3 (CH), 130.6 (CH), 129.8 (CH), 128.8 (CH), 115.2 (CH), 113.4 (C_Q), 113.0 (CH), 112.6 (C_Q), 111.4 (C_Q), 98.8 (C_Q), 95.2 (C_Q), 52.6 (C_Q), 25.9 (CH_3), 23.5 (CH_3). ?$_{max}$ (DMF) 526 $\log_{10}$e 5.00.

{4-(6-Acetanilido-*trans,trans*-1,3,5-hexatrienyl)-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}-propanedinitrile was purified by recrystallisation from acetic anhydride as a purple crystalline solid (**xx %**), m.p. 259-260 °C. (Found: MH^+ *m/z* 397.16590; $C_{24}H_{20}N_4O_2$ requires MH^+ *m/z* 397.16535; ? = 1.4 ppm). ^1H NMR (d_6-DMSO) d 8.04 (d, *J* 13.8 Hz, 1H), 7.70-7.47 (m, 4H), 7.60 (m, 1H), 7.37 (d, *J* 6.9 Hz, 2H), 7.30 (dd, *J* 14.4, 11.7 Hz, 1H), 6.45 (dd, *J* 14.1, 11.4 Hz, 1H), 6.42 (d, *J* 15.3 Hz, 1H), 5.18 (dd, *J* 13.8, 11.1 Hz, 1H), 1.92 (s, 3H), 1.69 (s, 6H). ^{13}C NMR (d_6-DMSO) 177.4 (C_Q), 175.4(C_Q), 169.2(C_Q), 150.3(CH), 148.2(CH), 139.8(CH), 138.7(C_Q), 130.6 (CH), 129.6 (CH), 128.9 (CH), 116.1 (CH), 113.4(C_Q), 112.9, 112.6(C_Q), 111.6(C_Q), 98.8(C_Q), 96.2(C_Q), 53.5(C_Q), 25.8 (CH_3), 23.4 (CH_3). $?_{max}$ (DMF) 628 $\log_{10}e$ 5.02.

{4-[(3-Acetanilidomethylene)-2-chloro-1-cyclohexen-1-yl]-*trans*-ethenyl-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile was recovered from the reaction mixture, washed with both acetic anhydride and then isopropanol and then dried to give the title compound as a purple crystalline solid (**xx %**), m.p. 225-227 °C. (Found: MH^+ *m/z* 471.15925; $C_{27}H_{23}N_4O_2$ Cl requires MH^+ *m/z* 471.15823; ? = 2.1 ppm). ^1H NMR (d_6-DMSO) d 8.42 (d, *J* 16.0 Hz, 1H), 7.91 (s, 1H), 7.55-7.43 (m, 5H), 6.68 (d, *J* 16.0 Hz, 1H), 2.53, (m, 2H), 1.90 (m, 2H), 1.83 (s, 6H), 1.60 (m, 2H). ^{13}C NMR (d_6-DMSO) 144.8 (CH), 134.8 (CH), 130.8 (C_Q), 129.5 (CH), 128.9 (CH), 117.1 (CH), 99.8 (C_Q), 27.5 (CH_2), 26.3 (CH_3), 21.9 (CH_2). No other lines were visible. $?_{max}$ (DMF) 502 $\log_{10}e$ 4.64.

{4-(2-Acetanilidoethenyl)-5-(4-acetoxyphenyl)-3-cyano-5-methyl-2(5*H*)-furanylidene}-propanedinitrile (5) was recovered by flash chromatography over silica (40 % ethyl acetate/hexanes) and recrystallised from acetone/hexane to give yellow prisms (**xx %**), m.p. 253-256 °C (decomp.). ^1H NMR (d_6-acetone) d 8.44 (d, *J* 14.2 Hz,1H), 7.67-7.60 (m, 5H), 7.43-7.41 (m,2H), 7.28 (d *J* 8.7 Hz, 2H), 5.29 (d, *J* 14.2 Hz, 1H), 2.30 (s, 3H), 2.23 (s,3H), 1.96 (s, 3H). ^{13}C NMR (d_6-acetone) 147.0 (CH), 131.9 (CH), 129.6 (CH), 129.0 (CH), 124.0 (CH), 100.8 (CH), 25.1 (CH_3), 23.9 (CH_3), 21.5 (CH_3). No other lines were visible. $?_{max}$ (DMF) 434 $\log_{10}e$ 4.78.

{4-[4-Acetanilido-*trans*-1,3-butadienyl]- 5-(4-acetoxyphenyl)-3-cyano-5-methyl-2(5*H*)-furanylidene}propanedinitrile (6) was recovered by flash chromatography over silica (30 % acetone/hexanes) and isolated as maroon prisms (68 %), m.p. 219-220 °C. (Found: C; 71.17, H; 4.25, N; 11.66. $C_{29}H_{22}N_4O_4$ requires C; 71.02, H; 4.49, N; 11.43 %. Found: MH^+ *m/z* 491.17167 $C_{29}H_{22}N_4O_4$ requires MH^+ *m/z* 491.17138; ? = 0.6 ppm). ^{1}H NMR (d_6-acetone) d 8.15 (d, *J* 13.6 Hz, 1H), 7.63-7.20 (m, 9H), 7.48 (bd dd, 1H), 6.39 (d, *J* 15.3 Hz, 1H), 5.39 (dd, *J* 13.6, 11.4 Hz, 1H), 2.27 (s, 6H), 1.92 (s, 3H). ^{13}C NMR (d_6-acetone) 178.0 (C_Q), 175.1 (C_Q), 170.1 (C_Q), 169.8(C_Q), 153.5 (C_Q), 151.9 (CH), 145.0 (CH), 139.7 (C_Q), 135.0 (C_Q), 131.7 (CH), 130.8 (CH), 129.8 (CH), 129.2 (CH),123.8 (CH), 116.5 (CH), 113.5 (CH), 112.9 (C_Q), 111.9 (C_Q), 100.0 (C_Q), 24.5 (CH_3), 23.7 (CH_3), 21.4 (CH_3). $?_{max}$ (DMF) 530 $\log_{10}$e 4.99.

Synthesis of p-bridged pyridinylidene and quinolinylidene 2(5*H*)-furanylidene}propanedinitrile optophores (7-15): General Condensation Procedures.

Method A: Equimolar quantities of the appropriate N-methylazinium halide (**12a**, **15**, or **16**), the *oligo*enamido acceptor (XX-XX) and triethylamine were dissolved in acetic anhydride (10 ml/mmol) and the solution refluxed for 5-10 min before being allowed to cool slowly. Crystalline adducts were recovered by filtration and washed thoroughly with fresh acetic anhydride followed by copious quantities of water and then isopropanol and then dried. Yields were consistently in excess of 60 %.

Method B: As for Method A, but with methanol as the solvent instead of acetic anhydride. This method was used for reactions with the azinium halides **12b** or **14**.

Method C: Equimolar quantities of N-(2,3-dihydroxypropyl)-4-picolonium chloride (B) (ref) and the *oligo*enamido acceptor were treated with catalytic triethylamine in refluxing acetic anhydride as described above. The cooled reaction mixtures were poured into ether (*c.* 25 ml/mmol reagent) and stirred vigorously for several minutes. The liquors were decanted and the oily residues washed by stirring with further portions of ether. The residual insoluble oils were stirred vigorously with aqueous sodium hydroxide solution (2 % w/v, 25 ml/mmol) at 90 °C for 30 min and the resulting solids recovered by filtration and

washed with water (to neutrality) followed by isopropanol and then dried. Yields of the optophores recovered in this manner were again in excess of 55 %.

(i) N-Methylpyridin-4(1*H*)-ylidene donors – Method A

4{2-(1-Methylpyridin-4(1*H*)-ylidene)ethenyl}-3-cyano-5,5-dimethyl-2(5*H*)furanylidene}-propanedinitrile (7) was obtained as a grey/green microcrystalline solid (xx %), m.p.> 300 °C. Found: MH^+ *m/z* 317.13969 $C_{19}H_{17}N_4O$ requires MH^+ *m/z* 317.13910; ? = 1.8 ppm). ^1H NMR (d_6-DMSO) d 8.48 (d, *J* 6.9 Hz, 1H), 8.41 (d, *J* 7.0 Hz, 1H), 8.35 (dd, *J* 14.8, 12.7 Hz, 0.5H), 7.86 (d, *J* 7.0 Hz, 1H), 7.63 (dd, *J* 14.4,12.7 Hz, 0.5H), 7.53 (d *J* 7.0 Hz, 1H), 6.34 (d *J* 14.5 Hz, 0.5H), 6.28 (d, *J* 14.8 Hz, 0.5H), 5.73 (d, *J* 12.5 Hz, 0.5H), 5.65 (d, *J* 12.1 Hz, 0.5H), 4.07 (s, 3H), 1.66 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (d_6-DMSO) 160.5 (C_Q), 159.4 (C_Q), 153.3 C_Q), 144.1 (CH), 143.6 (CH), 138.3 (CH), 138.2 (CH), 121.5 (CH), 120.7 (CH), 118.6 (CH), 117.6 (CH), 116.8 (C_Q), 115.4 (C_Q), 104.6 (CH), 103.9 (CH), 92.9 (C_Q), 92.6 (C_Q), 46.2 (CH_3), 46.1 (CH_3), 27.6 (CH_3), 27.4 (CH_3).
$?_{max}$ (DMF) 570 $\log_{10}e$ 4.86; (MeOH) 564; (pyridine) 600.

4{4-(1-Methylpyridin-4(1*H*)-ylidene)-1,3-butadienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (8) was obtained as a purple-blue powder (xx %), 282-284 °C. (Found: C; 73.12, H; 5.40 N; 16.25 $C_{21}H_{18}N_4O$ requires C; 73.60, H; 5.20, N; 16.36 %. Found: MH^+ *m/z* 343.15534 $C_{21}H_{19}N_4O$ requires MH^+ *m/z* 343.15484 ? = 1.4 ppm). ^1H NMR (d_6-DMSO) d 8.53 (d, *J* ca 6.9 Hz, 2H), 7.96 (d, *J* 6.9 Hz, 1H), 7.81 (d, *J* 6.7 Hz, 1H), 7.80 (t, *J* 13.2 Hz, 0.5H), 7.60 (m, 1H), 7.07 (t, *J* 13.2 Hz, 0.5H), 6.59 (d, *J* 15.3 Hz. 0.5 H), 6.51 (d, *J* 15.3 Hz, 0.5 H), 6.29 (m, 1H), 5.64 (d, *J* 12.9 Hz, 0.5 H), 5.53 (d, *J* 12.3 Hz, 0.5H), 4.1 (s, 3H), 1.60 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (d_6-DMSO) 156.5 (C_Q), 154.3 (C_Q), 153.2 (C_Q), 153.1 (C_Q), 144.7(CH), 143.5(CH), 139.9 (CH), 139.0 (CH), 125.9 (CH), 125.1 (CH),121.7 (CH),121.5 (CH), 120.5 (CH), 118.1 (C_Q), 115.8 (C_Q),105.2 (CH),104.9 (CH), 92.2 (C_Q), 91.8 (C_Q), 46.4 (CH_3), 27.6 (CH_3), 27.3 (CH_3). $?_{max}$ (DMF) 600 $\log_{10}e$ 4.78; (MeOH) 592; (pyridine) 670.

4{6-(1-Methylpyridin-4(1*H*)-ylidene)-1,3,5-hexatrienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (9) was obtained as a dark green powder (xx %), m.p. 231-233 °C. (Found: MH^+ *m/z* 369.17099 $C_{23}H_{20}N_4O$ requires MH^+ *m/z* 369.16929 ? = 4.6 ppm). ^1H NMR (d_6-DMSO) d 8.61 (bd t, *J* 6.4 Hz, 2H), 7.91 (bd t, *J* 6.2 Hz, 2H), 7.74 and 7.63 (2 x dd *J* 15.2,11.2 Hz and 15.0, 11.3 Hz respectively, approx 2:1 in intensity, 1H), 7.41 (bd t or dd, *J* 13.0 Hz, 0.67H), 6.96- 6.73 (m, 1.5H), 6.59 (bd d, *J* 16.4 Hz, 1H),6.42 (bd dd, *J* 14.10, 11.4 Hz,1H), 6.19 (bd 'q', *J* 13.4Hz, 1H), 5.57 and 5.46 (2 x d, *J* 12.6 and 12.1 Hz respectively, approx 1:2 in intensity, 1H), 4.1 (s, 3H), 1.56 and 1.37 (2 x s, approx 1:2 in intensity, 6H). Solvent insolubility precluded the recording of meaningful ^{13}C NMR data. $?_{max}$ (DMF) 615 $\log_{10}e$ 4.76; **(MeOH) xxx; (pyridine) xxx.**.

(ii) N-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene donors – Method C.

4{2-[(2,3-Dihydroxypropyl)pyridine-4(1*H*)-ylidene]ethenyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (10) was obtained as a xxx powder (xx %), m.p. 281-283 °C. (Found: MH^+ *m/z* 377.16082 $C_{21}H_{21}N_4O_3$ requires MH^+ *m/z* 377.16085 ? = 0.1 ppm). ^1H NMR (d_6-DMSO), isomer 1, d 8.79 (d, *J* 6.6 Hz, 1H), 8.37 (dd *J* 14.7, 12.0 Hz, 0.5H), 7.53 (d, *J* 6.6 Hz, 1H), 6.29 (d, *J* 14.7 Hz, 0.5H), 5.67 (d, *J* 12.0 Hz, 0.5 H), 1.44 (s, 3H); isomer 2, d 8.37 (d *J* 6.6 Hz, 1H), 7.86 (d *J* 6.6 Hz, 1H), 7.61 (dd, *J* 14.4, 12.9 Hz, 0.5H), 6.36 (d, *J* 14.4 Hz, 0.5 H), 5.76 (d, *J* 12.3 Hz, 0.5H), 1.67 (s, 3H). Resonances attributable to the dihydroxypropyl substituent were coincident for each isomer at d 5.34 (dd, *J* 7.2,5.7 Hz, 1H, $-CH_2OH$), 4.96 (t *J* 5.4 Hz, 1H, -CHO*H*), 4.48 (dd, *J* 13.6, 3.0 Hz, 1H, lower field branch of AB quartet, $-NCH_2$), 4.20 (m, 1H, higher field branch of AB quartet, $-NCH_2$), 3.83 (bd m, 1H, -C*H*OH), 3.48 (m, 1H, lower field branch of AB quartet, $-CH_2OH$), 3.33 (m, 1H, higher field branch of AB quartet, $-CH_2OH$). ^{13}C NMR (d_6-DMSO, no quaternary resonances cited) 144.0 (py-CH), 143.5 (py-CH), 138.6 (CH), 138.5 (CH), 121.2 (py-CH), 120.4 (py-CH), 118.5 (CH), 117.6 (CH), 104.6 (CH), 104.0 (CH), 70.8 (CH), 63.3 (CH_2), 62.1 (CH_2), 27.6(CH_3), 27.4(CH_3). $?_{max}$ (DMF) 572 $\log_{10}e$ 4.79; (MeOH) 570; (pyridine) 598.

4{4-[(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]-1,3-butadienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (11) was obtained as a xxx powder (xx %), **m.p. xxx** °C. (Found: MH^+ *m/z* 403.17832 $C_{23}H_{23}N_4O_3$ requires MH^+ *m/z* 403.17789 ? = 3.5 ppm). ^1H NMR (d_6-DMSO) two isomers, approximately 1:1, d 8.51 (bd d, *c.*7 Hz, 2H), 7.96 (d, *J* 6.9 Hz, 1H), 7.80 (d + m, *J* 6.9 Hz, 1.5H), 7.65 (m, 1H), 7.09 (t, *J* 13.2 Hz, 0.5H), 6.50 (2 x d, *J* 14.8, 14.5 Hz, 1H), 6.35 (bd 'q', *J* 11.5 Hz, 1H), 5.66 (d, *J* 12.8 Hz, 0.5 H), 5.53 (d, *J* 12.2 Hz, 0.5 H), 5.35 (bd s, 1H, -OH), 4.96 (bd s, 1H, -OH), 4.52 (bd d, *J c.* 13 Hz, 1H, lower field branch of AB quartet, $-NCH_2$), 4.22 (m, 1H, higher field branch of AB quartet, $-NCH_2$), 3.84 (bd 's', 1H, -C*H*OH), 3.48 (m, 1H, lower field branch of AB quartet, $-CH_2OH$), 3.33 (m,1H, higher field branch of AB quartet, $-CH_2OH$), 1.60 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (d_6-DMSO, no quaternary resonances cited) 144.9 (CH), 144.1 (2py-CH), 143.7 (CH), 140.0 (CH), 139.2(CH), 126.0 (py-CH), 125.2 (py-CH), 122.0 (CH), 121.4 (CH), 120.5 (CH), 105.3 (CH), 105.0 (CH), 70.8 (CH), 63.3 (CH_2), 62.3 (CH_2), 27.6 (CH_3), 27.3 (CH_3). $?_{max}$ (DMF) 604 $\log_{10}e$ 4.64; (MeOH) 598; (pyridine) 662.

(iii) N-Methylpyridin-2(1*H*)-ylidene donors – Method A

4{2-(1-Methylpyridin-2(1*H*)-ylidene)ethenyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (XX) was obtained as a xxx powder, **(xx %), m.p. xxx** °C. (Found: MH^+ *m/z* 317.13969 $C_{19}H_{17}N_4O$ requires MH^+ *m/z* 317.13808; ? = 5.1 ppm). ^1H NMR (d_6-DMSO) two isomers, approximately 1:1, isomer 1 d 8.57 (d, *J* 6.0 Hz, 0.5H), 8.41 (d, *J* 7.9 Hz, 0.5H), 8.21 (t, *J* 7.8 Hz, 0.5H), 7.67 (dd, *J* 13.8,12.8 Hz, 0.5H), 7.46 (t, *J* 7.8 Hz, 0.5H), 6.55 (d, *J* 14.1 Hz, 0.5H), 5.93 (d, *J* 12.5 Hz, 0.5H); isomer 2 d 8.51 (d, *J* 6.0 Hz, 0.5H), 8.38 (dd, *J* 14.4,12.1 Hz, 0.5 H), 8.07 (t, *J* 7.8 Hz, 0.5H), 7.79 (d, *J* 8.3 Hz, 0.5H), 7.41 (t, *J* 6.9 Hz, 0.5 H), 6.44 (d, *J* 14.4 Hz, 0.5H), 5.76 (d, *J* 12.1 Hz, 0.5H), 4.31/4.32 (2 x s, 3H), 1.67/1.45 (2 x s, 6H). ^{13}C NMR (d_6-DMSO) 176.5 (C_Q), 174.8 (C_Q), 161.7 (C_Q), 160.4 (C_Q), 153.4 (C_Q), 153.2 (C_Q), 145.1(CH), 144.7 (CH), 142.6 (CH), 141.7 (CH), 140.1 (CH), 123.5 (CH), 122.0 (CH), 121.2 (CH), 120.9 (CH), 118.2 (C_Q), 117.6 (C_Q), 116.9 (C_Q), 116.6 (C_Q), 115.4 (C_Q), 110.9 (CH), 110.4 (CH), 104.7 (CH), 103.9 (CH), 93.0 (C_Q), 92.7 (C_Q), 75.2 (C_Q), 71.6 (C_Q), 45.3 (CH_3), 27.6 (CH_3), 27.4 (CH_3). $?_{max}$ (DMF) 556 $\log_{10}e$ 4.90; (MeOH) 550; (pyridine) 580.

4{2-(1-Methylpyridin-2(1*H*)-ylidene)-1,3-butadienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (XX) was obtained as a xxx powder, **(xx %), m.p. xxx °C.** (Found: MH^+ *m/z* 343.15534 $C_{19}H_{17}N_4O$ requires MH^+ *m/z* 343.15654; ? = 3.5 ppm). ^1H NMR (d_6-DMSO) two isomers, approximately 1:1, d 8.62 (m, 1H), 8.44 (d, *J* 7.1 Hz, 0.5H), 8.20 (m, 1.5H), 7.88 (dd, *J* 14.7,11.3 Hz, 0.5H), 7.75-7.48 (m, 2H), 7.16 ('t', *J* 13.3 Hz, 0.5H), 6.64 ('t', *J* 15.1 Hz, 1H), 6.36 (m, 1H), 5.65 (d, *J* 12.8 Hz, 0.5H), 5.53 (d, *J* 12.2 Hz, 0.5H), 4.13/4.12 (2 x s, 3H), 1.61, 1.41 (2 x s, 6H). ^{13}C NMR (d_6-DMSO) 175.7 (C_Q),173.9 (C_Q), 157.5 (C_Q),155.2 (C_Q),153.2 (C_Q), 152.1 (C_Q), 146.7 (CH), 145.5 (CH), 145.3 (CH), 142.7 (CH), 142.5 (CH), 141.1 (CH), 140.1 (CH), 125.7 (CH), 124.8 (CH), 123.9 (CH), 123.1 (CH), 122.5 (CH), 122.1 (CH),118.0 (C_Q), 117.4 (C_Q), 115.7 (C_Q), 114.2 (CH), 113.1 (CH), 105.0 (CH), 104.7 (CH), 92.3 (C_Q),92.0 (C_Q), 74.2(C_Q), 70.1 (C_Q), 45.5 (CH_3), 27.6 (CH_3), 27.3 (CH_3). $?_{max}$ (DMF) 588 $\log_{10}e$ 4.81; (MeOH) 582; (pyridine) 662.

4{6-(1-Methylpyridin-2(1*H*)-ylidene)-1,3,5-hexatrienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (xx) was obtained as a red-brown solid, **(xx %)**, m.p. 200-202 (partial) **°C.** (Found: MH^+ *m/z* 369.17099 $C_{23}H_{21}N_4O$ requires MH^+ *m/z* 369.17246; ? = 4.0 ppm). Solvent insolubility precluded the recording of meaningful ^1H and ^{13}C NMR data although it was possible to discern the presence of predominantly two isomers (2:1) principally from the two doublets at d 5.59 and 5.48, the two N-CH_3 singlets at d 4.22 and 4.16 and the two *gem*-methyl singlets at d 1.56 and 1.37. $?_{max}$ 598 (DMF) $\log_{10}e$ 4.29.

(iv) N-(2,3-dihydroxypropyl)pyridin-2(1*H*)-ylidene donors – Method C

4{2-(2,3-Dihydroxypropyl)pyridin-2(1*H*)-ylidene)ethenyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (XX) was obtained as a **xxx** powder, **(xx %), m.p. xxx °C. (Found: MH^+ *m/z* $C_{21}H_{20}N_4O_3$ requires MH^+ *m/z* 317.13808; ? = 5.1 ppm).** ^1H NMR (d_6-DMSO) two isomers, approximately 1:1; d 8.50-8.33 (m, 2H), 8.23 (t, *J* 7.9 Hz, 0.5H), 8.09 (t, *J* 7.8 Hz, 0.5H), 7.83 (d, *J* 8.4 Hz, 0.5H), 7.66 ('t', *J* 13.3 Hz, 0.5H), 7.50 (t, *J* 6.9 Hz, 0.5H), 7.44 (t, *J* 6.8 Hz, 0.5H), 6.59 (d, *J* 14.1 Hz, 0.5H), 6.52 (d, *J* 14.4 Hz, 0.5H), 5.90 (d, *J* 12.5 Hz, 0.5H), 5.72 (d, *J* 12.1 Hz, 0.5H), 5.31 (m, 1H), 5.01

(m, 1H) 4.74 (bd t, *J* 10.9 Hz, lower field branch of AB quartet, 1H),4.22 (m, higher field branch of AB quartet, 1H),3.84 (bd m, 1H), 3.53 (m, lower field branch of AB quartet, 1H), 3.46 (m, higher field branch of AB quartet, 1H), 1.67 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (d_6-DMSO) 176.5 (C_Q), 174.8 (C_Q), 161.4 (C_Q), 160.1 (C_Q), 153.3 (C_Q), 152.8 (C_Q), 145.8, (CH), 145.5 (CH), 142.8 (CH), 141.9 (CH),140.2 (CH), 139.9 (CH), 123.9 (CH), 122.5 (CH), 121.0 (CH), 120.6 (CH), 118.3 (C_Q), 117.6 (C_Q),116.7 (C_Q),, 115.4 (C_Q), 110.8 (CH), 110.3 (CH), 104.7 (CH), 103.8 (CH), 92.9 (C_Q), 92.7, (C_Q), 75.0 (C_Q), 71.5 (C_Q), 69.6 (CH), 63.7 (CH_2), 60.0 (CH_2), 59.8 (CH_2), 27.7 (CH_3), 27.4 (CH_3). ?$_{max}$ 556 (DMF) $\log_{10}$e 4.72; (MeOH) 552; (pyridine) 578

4{4-(2,3-Dihydroxypropyl)pyridin-2(1*H*)-ylidene)-1,3-butadienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (xx) was obtained as a xxx microcrystalline solid, (xx %), **m.p. xxx °C. (Found: MH$^+$ *m/z* $C_{23}H_{22}N_4O_3$ requires MH$^+$ *m/z* ; ? = ppm).** ^{1}H NMR (d_6-DMSO) two isomers, approximately 1:1; d 8.49 (m, 2H), 8.21 (m, 1.5H), 7.86 (dd, *J* 14.6, 11.3 Hz, 0.5 H), 7.78-7.49 (m, 2.5H), 7.16 (t, *J* 13.3 Hz, 0.5H)6.72 (dd, *J* 14.5, 11.4 Hz, 1H), 6.33 (m, 1H), 5.65 (d, *J* 12.8 Hz, 0.5H), 5.53 (d, *J* 12.2 Hz, 0.5H), 5.33 (m,1H), 5.04 (m,1H), 4.78 (m, lower field branch of AB quartet, 1H), 4.25 (m, higher field branch of AB quartet, 1H), 3.82 (m, 1H), 3.54 (m, lower field branch of AB quartet, 1H), 3.44 (m, higher field branch of AB quartet, 1H) 1.61 (s, 3H), 1.40 (s,3H). Solvent insolubility precluded the recording of meaningful ^{13}C NMR data.). ?$_{max}$ (DMF) 590 $\log_{10}$e 4.61; (MeOH) 584; (pyridine) 652.

(v) N-(2-Hydroxyethyl)quinolin-4(1*H*)-ylidene donors – Method B

4{2-[(2-Hydroxyethyl)quinolin-4(1*H*)-ylidene]ethenyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile ( ) was obtained as a ??? microcrystalline solid, (xx %), **m.p. xxx °C.** (Found: MH$^+$ *m/z* **397.** $C_{24}H_{20}N_4O_2$ **requires MH$^+$ *m/z* 397.16964 ? = ppm).** ^{1}H NMR (d_6-DMSO) two isomers, approximately 1:1 d 8.77-8.45 (m, 2.5H), 8.34-7.70 (m, 4H), 7.48 (d, *J* 6.3 Hz, 0.5H), 7.32 (d, *J* 13.3 Hz, 0.5H), 7.21 (d, *J* 14.0 Hz, 0.5H), 6.16 (d, *J* 12.7 Hz, 0.5 H), 5.94 (d, *J* 12.3 Hz, 0.5H), 5.10 (bd s, 1H), 4.77 (bd 's', 2H), 3.85 (bd 's', 2H), 1.74 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (d_6-DMSO) 175.3

(C_Q), 163.9 (C_Q), 162.6 (C_Q), 152.5 (C_Q), 152.4 (C_Q), 146.0 (CH), 145.1 (CH), 141.3 (CH), 138.5 (C_Q), 134.1 (CH), 134.0 (CH), 128.0 (CH), 127.7 (CH), 126.2 (CH), 125.9 (CH), 125.6 (C_Q), 119.0 (CH), 118.7 (CH), 117.9 (C_Q), 117.1 (C_Q), 116.3 (C_Q), 114.5 (CH), 113.6 (CH), 112.1 (CH), 110.9 (CH), 106.8 (CH), 105.8 (CH), 93.6 (C_Q), 59.3 (CH_2), 57.7 (CH_2), 57.4 (CH_2), 27.7 (CH_3), 27.2 (CH_3). $?_{max}$ (DMF) 660 $\log_{10}e$ 5.00; (MeOH) 654; (pyridine) 682.

4{4-[(2-Hydroxyethyl)quinolin-4(1*H*)-ylidene]-1,3-butadienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (XX) was obtained as a **???** microcrystalline solid, **(xx %), m.p. xxx °C. (Found: MH^+ *m/z* 423. $C_{26}H_{22}N_4O_2$ requires MH^+ *m/z* 423. ? = ppm).** ^{1}H NMR (d_6-DMSO) two isomers, approximately 1:1 d 8.74 (d, *J* 6.8 Hz, 1H), 8.67 (bd 's', 1H),8.45-7.69 (m, 5H), 7.59-7.22 (m,2H), 6.51 (dd, *J* 13.3,12.0 Hz,1H), 5.77 (d, *J* 12.6 Hz, 0.5H),5.65 (d, *J* 12.1Hz.0.5H), 5.13 (t, *J* 5.4 Hz,1H), 4.84 (bd s,2H), 3.86 (m,2H), 1.65 (bd s ,3H), 1.44 (bd s, 3H). Solvent insolubility precluded the recording of meaningful ^{13}C NMR data. $?_{max}$ (DMF) 735 $\log_{10}e$ 4.88; (MeOH) 724; (pyridine) 782.

4{6-[(2-Hydroxyethyl)quinolin-4(1*H*)-ylidene]-1,3,5-hexatrienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (XX) was obtained as a **???** microcrystalline solid, **(xx %), m.p. xxx °C. (Found: MH^+ *m/z* 448. $C_{28}H_{24}N_4O_2$ requires MH^+ *m/z* 448. ? = ppm).** ^{1}H NMR (d_6-DMSO) two isomers, approximately 2:1 d 8.89 (bd s, 1H), 8.71 (d, *J* 8.51 Hz, 1H), 8.40 (d, *J* 8.9 Hz, 1H), 8.14-7.90 (m, 4H), 7.56 (d+ v bd m, *J* 14.6 Hz, 2H), 7.01 (bd m, 1H), 6.65 (dd, *J* 13.9,11.5, 1H), 6.27 bd t, *J* 12.4 Hz, 1H), 5.57 (bd m, 1H), 5.12 (t, *J* 5.2 Hz, 1H), 4.90 (bd 's', 2H), 3.90 (bd 's', 2H), 1.58 (bd s, 3H), 1.40 (bd s, 3H). ^{13}C NMR (d_6-DMSO) 175.3 (C_Q), 153.7 (C_Q), 152.5(C_Q), 146.9 (CH), 146.2 (CH), 138.5 (C_Q), 137.6 (CH), 134.6 (CH), 128.7 (CH), 126.2 (CH), 119.3 (CH), 118.4 (C_Q), 113.8 (CH), 105.7 (CH), 92.1 (C_Q), 59.3 (CH_2), 58.4 (CH_2), 27.6 (CH_3). $?_{max}$ 735 (DMF) $\log_{10}e$ 4.70; (MeOH) 705; (pyridine) 860.

4-{2-[4-(2-Hydroxyethyl)quinolin-4(1*H*)-ylidene]-ethylidene)-2-chloro-1-cyclohexen-1-yl]-*trans*-ethenyl]-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene propanedinitrile (XX) was recovered as a grey/green microcrystalline solid, (xx %), **m.p. xxx °C** ^{1}H NMR (d_6-DMSO) d 8.97 (d, *J* 6.6 Hz, 1H), 8.87 (d, *J* 8.5 Hz, 1H), 8.47 (d, *J* 8.9 Hz, 1H), 8.29 (d, *J* 15.3 Hz, 1H), 8.17 (t, *J* 7.8 Hz, 1H), 7.95 (t, *J* 7.7 Hz, 1H), 7.61 (d, *J* 15.3 Hz, 1H) 7.30 (apparent s, 1H), 5.66 (bd, 1H), 5.14 (bd t, -O*H*), 4.98 (bd t, 2H), 3.90 (m, 2H), 2.79 (m, 2H), 2.59 (m, 2H), 1.86 (m, 2H), 1.47 (bd s, 6H). ^{13}C NMR (d_6-DMSO) 152.6 (C_Q), 147.8 (CH), 140.3 (CH), 138.4 (C_Q), 134.8 (CH), 130.0 (C_Q), 129.1(CH), 126.8 (CH), 119.4 (CH), 118.9 (CH), 117.5 (C_Q), 115.4 (CH), 101.9 (CH), 59.3 (CH_2), 58.8 (CH_2), 27.6 (CH_3), 27.3 (CH_3), 26.2 (CH_2), 21.2 (CH_2). ?$_{max}$ xxx (DMF) $\log_{10}$e xxx; (MeOH) 710; (pyridine) 865.

(vi) N-Methylquinolin-2(1*H*)-ylidene donors – Method A

4{2-[1-Methylquinolin-2(1*H*)-ylidene]ethenyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (xx) was obtained as a ??? microcrystalline solid, (xx %), **m.p. xxx °C.** (Found: MH^+ *m/z* 367.15534; $C_{23}H_{18}N_4O$ requires MH^+ *m/z* 367.15368 ? = 4.5 ppm). ^{1}H NMR (d_6-DMSO) two isomers, approximately 2:1, d 8.70 (bd m, 0.3H), 8.49 (bd m, 0.3H), 8.35 (bd m, 1H), 8.15 (bd m, 1H), 8.04 (dd, *J* 7.9,1.2 Hz, 1H), 7.92 (bd m, 1.3H), 7.74 (bd m, 0.3H), 7.65 (bd m, 1H), 6.80 (d, *J* 13.5 Hz, 0.6H), 6.69 (d, *J* 12.6 Hz, 0.3H),6.19 (d, *J* 13.0 Hz, 0.6H), 5.98 (d, *J* 11.8 Hz, 0.3H), 41.3 (bd s, 3H), 1.75 (s, 4H), 1.51 (bd s, 2H). Solvent insolubility precluded the recording of meaningful ^{13}C NMR data. ?$_{max}$ (DMF) 620 $\log_{10}$e 5.18; (MeOH) 610; (pyridine) 634.

4{4-[1-Methylquinolin-2(1*H*)-ylidene]-1,3-butadienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (XX) was obtained as a ??? microcrystalline solid, (xx %), **m.p. xxx °C.** (Found: MH^+ *m/z* 393.17099; $C_{25}H_{20}N_4O$ requires MH^+ *m/z* 393.17162 ? = 1.6 ppm). ^{1}H NMR (d_6-DMSO) two isomers, approximately 2:1, d 8.60–7.65 (5 x bd m, 8H), 6.89 (bd m, 1H), 6.51 (bd t, *J* 12.2 Hz, 1H), 5.78 (bd m, 1H), 4.15 (bd s, 3H), 1.65 (bd s, 4H), 1.47 (bd s, 2H). Solvent insolubility precluded the recording of meaningful ^{13}C NMR data. ?$_{max}$ (DMF) 710 $\log_{10}$e 5.12; (MeOH) 700; (pyridine) 740.

4{6-[1-Methylquinolin-2(1*H*)-ylidene]-1,3,5-hexatrienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene}propanedinitrile (XX) was obtained as a emerald green powder, (xx %), m.p. 245-248 °C. (Found: MH^+ *m/z* 419.18664; $C_{27}H_{22}N_4O$ requires MH^+ *m/z* 418.18532 ? = 3.1 ppm). Solvent insolubility precluded the recording of meaningful ^1H and ^{13}C NMR data. $?_{max}$ 746 (DMF) $log_{10}e$ 4.85; (MeOH) 700; (pyridine) 850.

(vii) N-(2-Hydroxyethyl)benzothiazol-2(3*H*)-ylidene donors – Method B

4-[{2-[N-(2-hydroxyethyl)benzothiazol-2(3*H*)-ylidene]-ethenyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene propanedinitrile (XX) was recovered as a grey/green microcrystalline solid, (xx %), m.p. > 300 °C. (Found: MH^+ *m/z* 403.12232; $C_{22}H_{18}N_4O_2S$ requires MH^+ *m/z* 403.12398 ? = 4.1 ppm). ^1H NMR (d_6-DMSO) d 8.04 (d, *J* 5.8 Hz, 1H0, 7.82 (d, *J* 8.1 Hz, 1H), 7.61 (t, *J* 7.4 Hz, 1H), 7.48 (t, *J* 7.4 Hz, 1H), 6.68 (d, *J* 13.2 Hz, 1H), 6.00 (bd s, 1H), 4.64 (t, *J* 5.4 Hz, 2H), 4.07 (t, *J* 5.4 Hz, 2H), 1.62 (s, 6H). Solvent insolubility precluded the recording of meaningful ^{13}C NMR data. $?_{max}$ (DMF) 605 $log_{10}e$ 5.18; (MeOH) 598; (pyridine) 614.

4-[{4-[N-(2-hydroxyethyl)benzothiazol-2(3*H*)-ylidene]-1,3-butadienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene propanedinitrile (XX) was recovered as a grey/green microcrystalline solid, (xx %), m.p. 275 °C. (Found: MH^+ *m/z* 429.13797; $C_{24}H_{20}N_4O_2S$ requires MH^+ *m/z* 429.14030 ? = 5.4 ppm). ^1H NMR (d_6-DMSO) d 8.12 (d, *J* 7.8 Hz, 1H), 7.91 (d, *J* 8.3 Hz, 1H), 7.82 (bd m, 2H), 7.64 (t, *J* 8.2 Hz, 1H), 7.53 (t, *J* 7.7 Hz, 1H), 6.86 (d, *J* 13.9 Hz, 1H), 6.41 ('t', *J* 12.4 Hz, 1H), 5.84 (d, *J* 13.1 Hz, 1H), 5.08 (t, *J* 5.5 Hz, 1H), 4.61 (nm, 2H), 3.82 (nm, 2H), 1.62 (bd s, 6H). ^{13}C NMR (d_6-DMSO) 151.5 (CH), 147.4 (CH), 142.2 (C_Q), 128.6 (CH), 126.5 (CH), 124.1 (CH), 123.6 (CH), 116.8 (C_Q), 115.6 (CH), 107.2 (CH), 106.3 (CH), 94.1 (C_Q), 59.0 (CH_2), 50.1 (CH_2), 27.1 (CH_3). $?_{max}$ (DMF) 705 $log_{10}e$ 5.21; (MeOH) 698; (pyridine) 718.

4-{6-[N-(2-hydroxyethyl)benzothiazol-2(3*H*)-ylidene]-1,3,5-hexatrienyl}-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene propanedinitrile (XX) was recovered as a grey/green microcrystalline solid, (xx %), m.p. > 265 °C. (Found: M^+ *m/z* 454.14768; $C_{26}H_{22}N_4O_2S$

requires M^+ *m/z* 454.14580 ? = 4.1 ppm). ^{1}H NMR (d_6-DMSO) d 8.21 (d, *J* 7.8 Hz, 1H), 8.00 (d, *J* 8.4 Hz, 1H), 7.79 (bd m, *c.*1H), 7.70 (t, *J* 7.5 Hz, 1H), 7.61 (t, *J* 7.5 Hz, 1H), 7.59 (bd m, *c.*1H), 7.34 (bd m, *c.*1H), 7.10 (d, *J* 14.1 Hz, 1H), 6.53 ('t', *J* 12.6 Hz, 1H),6.34 (bd m, 1H), 5.71 (d, *J* 12.6 Hz, 1H), 5.18 (bd, 1H), 4.68 (nm, 2H), 3.84 (nm, 2H), 1.50 (bd s, 6H). Solvent insolubility precluded the recording of meaningful ^{13}C NMR data. $?_{max}$ 810 (DMF) $\log_{10}$e 4.91; (MeOH) 805; (pyridine) 830.

4-[{3-([N-(2-hydroxyethyl)benzothiazol-2(3*H*)-ylidene]ethylidene)-2-chloro-1-cyclohexen-1-yl]-*trans*-ethenyl]-3-cyano-5,5-dimethyl-2(5*H*)-furanylidene propanedinitrile (XX) was recovered as a grey/green microcrystalline solid, **(xx %), m.p. xxx °C.**

(Found:).

^{1}H NMR (d_6-DMSO) d 8.23 (d, *J* 7.4 Hz, 1H), 8.13 (d, *J* 14.7 Hz, 1H), 8.06 (d, *J* 8.3 Hz, 1H), 7.96 (m, 1H), 7.73 (t, *J* 8.3 Hz, 1H), 7.63 (t, *J* 7.4 Hz, 1H), 7.08 (d, *J* 14.7 Hz, 1H), 5.76 (d, *J* 13.2 Hz, 1H), 5.11 (t, *J* 5.9 Hz, 1H, O*H*), 4.81 (m, 2H), 3.85 (m, 2H), 2.65 (m, 2H), 2.60 (m, 2H), 1.81 (m, 2H), 1.53 (s,6H). Solvent insolubility precluded the recording of meaningful ^{13}C NMR data. $?_{max}$ 854 (DMF) $\log_{10}$e 4.91; (MeOH) 840; (pyridine) 865.

4-{4-[N-(2-hydroxyethyl)benzothiazol-2(3*H*)-ylidene]-1,3-butadienyl}-5-(4-acetoxy-phenyl)-3-cyano-5-methyl-2(5*H*)-furanylidene propanedinitrile (XX) was recovered as a grey/green microcrystalline solid, **(xx %)**, m.p. 257 °C. (Found: MH^+ *m/z* 549.16072; $C_{31}H_{24}N_4O_4S$ requires MH^+ *m/z* 549.15910 ? = 2.9 ppm). ^{1}H NMR (d_6-DMSO) d 8.13 (d, *J* 7.9 Hz, 1H), 7.94 (d, *J* 8.2 Hz, 1H), 7.75-7.40 (m, 6H), 7.21 (d, *J* 8.6 Hz, 2H) 6.90 (bd m, 1H), 6.35 ('t', *J* 12.3 Hz, 1H), 5.91 (bd m, 1H), 5.06 (t, *J* 5.4 Hz, 1H), 4.60 (nm, 2H), 3.81 (nm, 2H), 2.73 (s, 3H), 2.04 (v bd s, 3H). ^{13}C NMR (d_6-DMSO) 169.4 (C_Q), 151.1 (C_Q), 147.0 (C_Q), 142.1 (C_Q), 128.8 (CH), 127.8 (CH), 126.8 (CH), 124.7 (CH), 123.7 (CH), 122.5 (CH), 116.8 (C_Q), 116.0 (CH), 107.5 (CH), 106.5 (CH), 94.8 (C_Q), 59.1 (CH_2), 50.3 (CH_2), 25.1 (CH_3), 21.2 (CH_3). $?_{max}$ 705 (DMF) $\log_{10}$e 5.26.

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By the authorised agents
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Per Christine Kelly.

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